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(54) Recording film and recording method using the same

(57) A recording film suitable for dual recording first by ink jet patterning to form a base image pattern in a recording layer and then by a pen plotter to write an add-on information image thereon, consists of a substrate film, an ink-receptive layer on the substrate surface and a dot configuration-controlling layer on the ink-receptive layer. The ink-receptive layer is formed from a coating composition comprising a polyvinyl alcohol, a polyvinyl pyrrolidone, an inorganic powder such as a combination of silica and calcium carbonate powders for surface roughening, and a crosslinking agent such as a urea resin; while the dot configuration-controlling layer is formed from an acrylic resin of the quaternary ammonium salt type. The surface of the recording layer has a surface roughness of 0.8-1.5  $\mu\text{m}$ .

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FIG. 1

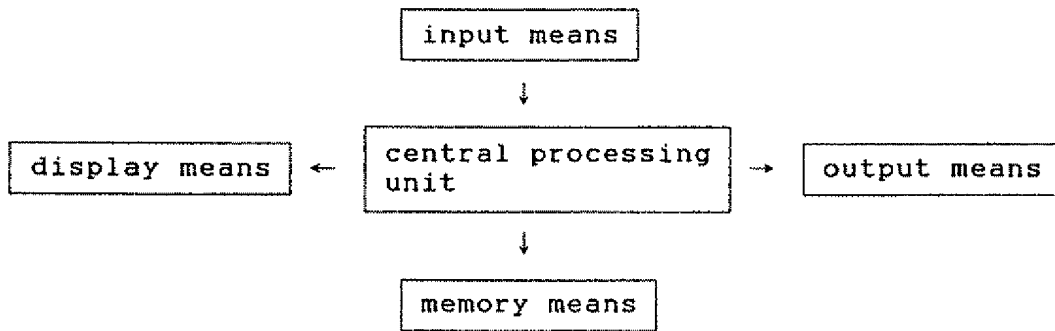


FIG. 2

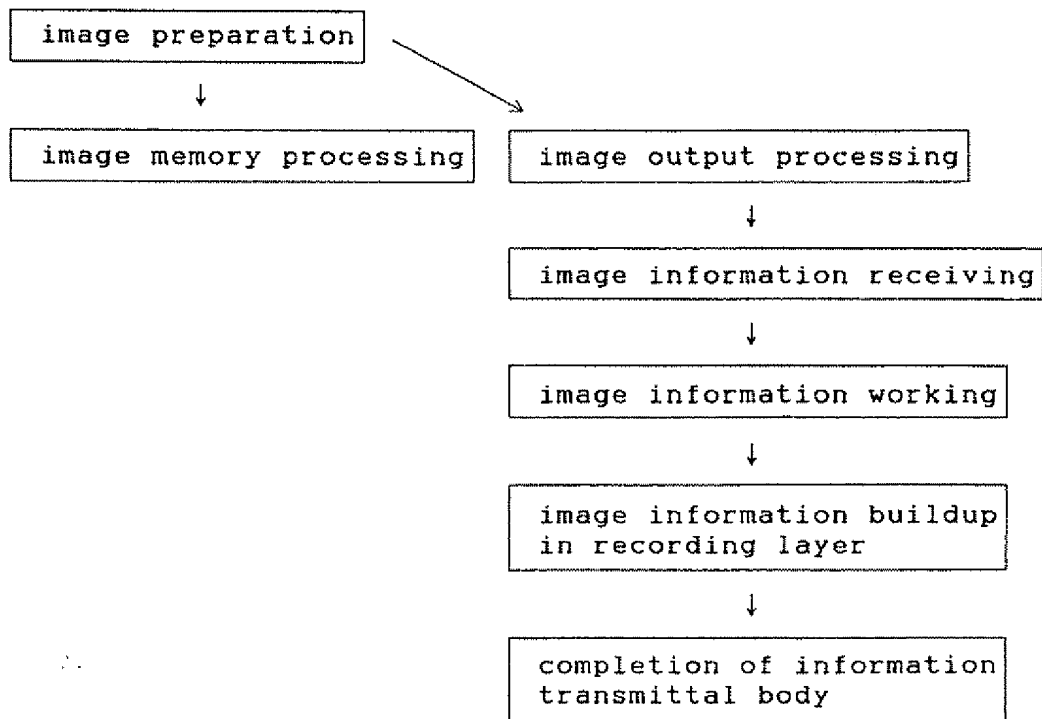
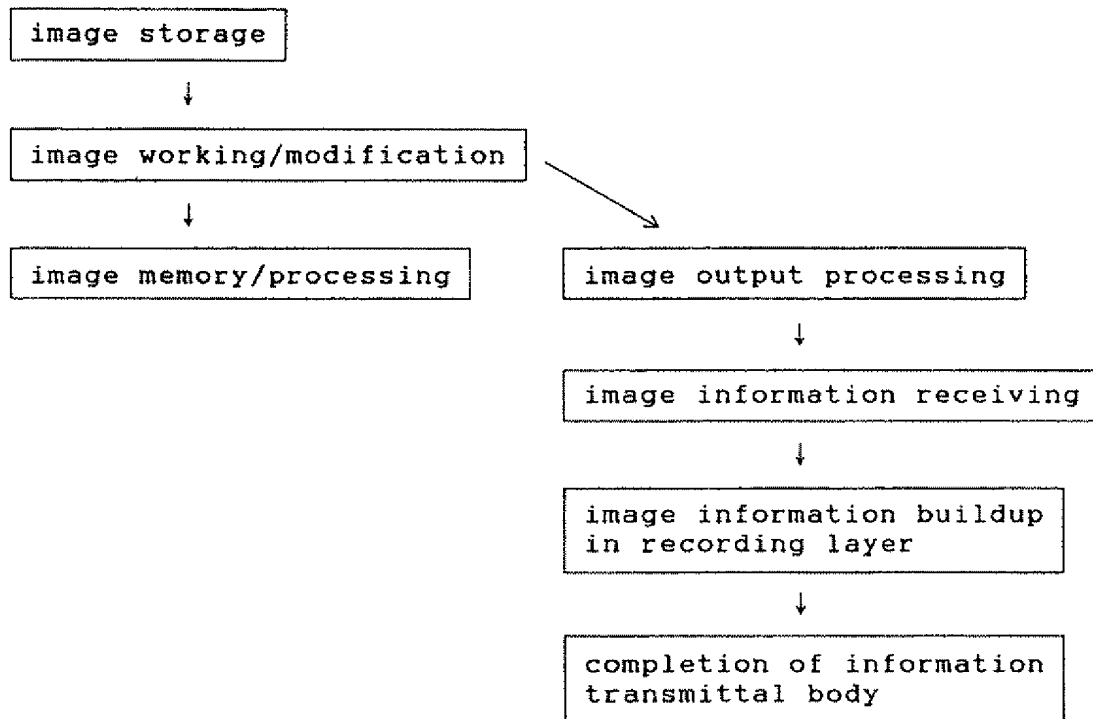


FIG. 3



RECORDING FILM AND RECORDING  
METHOD USING THE SAME

The present invention relates to a novel recording film and a method for recording using the same. More particularly, the invention relates to a  
5 recording film suitable for dual recording, in which a base image is first formed by ink jet plotting in the recording layer on a substrate and then a sharp add-on information image can be formed on the surface of the recording layer by pen plotting, as well as to a  
10 method of dual information recording using the recording film.

In the preparation of a development drawing or design drawing, it is usual in the prior art that a pattern of the base information is first formed on the  
15 recording material by using an ink jet plotter followed by a color coding operation using different colors. In the color coding operation here implied, taking a development drawing as an example, the present status of the working object and the next to  
20 final status thereof are indicated by using separate colors for clear recognizability. In a geographical map as another example, addresses, district names and so on are indicated by using different colors on a base drawing for clear recognizability. This color  
25 coding operation is traditionally undertaken manually after formation of the base drawing using a pen plotter, ink jet plotter or other writing means so that the color coding unavoidably has very low working efficiency and productivity.

30 It is a trend in recent years that the color coding operation of drawing is conducted using a computer. In the computerized color coding operation,

the portion to be color-coded is first formed in the computer and an output instrument such as an ink jet printer or ink jet plotter is operated on the base of the thus inputted information to record the  
5 color-coded information followed by recording of the desired add-on information by using a pen plotter. A great improvement can be accomplished by this means in the working efficiency and productivity of the color coding operation. The recording material used in this  
10 color coding operation is a substrate film which is provided on one surface with an ink-receptive layer consisting of a hydrophilic polymeric resin and a surface-roughness building powder (see, for example, Japanese Patent Kokai 7-195894).

15 A problem in the use of a conventional recording material for color coding is that, when the add-on information is recorded using a pen plotter after recording of the color-coded base pattern using an ink jet means, blurring or  
20 interruption of the line image is sometimes unavoidable which causes great difficulty in recording of the add-on information. When an improvement is attempted in the writing adaptability of the pen plotter, on the other hand, a decrease in  
25 reproducibility and coloration of the pattern to be recorded by the ink jet means is unavoidable.

The present invention accordingly has an object to provide, by overcoming the disadvantages and problems in the conventional recording material  
30 described above, a novel recording film in which a base image pattern is first recorded in the recording layer by an ink jet plotter or printer with excellent pattern reproduction and coloration and then a sharp add-on image pattern is recorded on  
35 the surface of the recording layer using a pen plotter. The invention also has an object to provide

a method for pattern recording using the above mentioned novel recording film.

Thus, the recording film provided by the invention, which is an integrally layered body,  
5 comprises:

(1) a substrate film; and

(2) a composite recording layer consisting of

(A) an ink-receptive layer formed on one surface  
of the substrate film, the layer consisting of a  
10 mixture of (a) a polyvinyl alcohol resin, (b) a  
polyvinyl pyrrolidone resin, (c) an inorganic powder  
for surface roughening and (d) a crosslinking agent,  
and

(B) an overcoating layer containing a dot  
15 configuration-controlling agent formed on the  
ink-receptive layer, the surface of the recording  
layer having a surface roughness in the range from  
0.8 to 1.5  $\mu\text{m}$ .

The method of the present invention for image  
20 pattern recording comprises the steps of:

i) forming a base image pattern in the recording  
layer of the above defined recording film by an ink  
jet patterning means; and

25 ii) forming an add-on image pattern on the surface  
of the recording layer by a pen plot patterning  
means.

In the drawings:

Figure 1 is a block diagram for the practice  
30 of the instrument system for the inventive method.

Figures 2 and 3 are each block diagrams of the  
process for the formation of an image pattern  
according to the invention.

The substrate film, on which the recording layer  
35 is formed to give the inventive recording film, is not  
particularly limitative and can be selected from those  
conventional polymeric resin films used in recording

films of the prior art. Examples of suitable polymeric material of the substrate film include polyethylene terephthalate resins, polyethylenes, polypropylenes and polyamide resins, of which  
5 polyethylene terephthalate resins are preferable. When the recording film bearing an image pattern is used as an image sheet of an overhead projector, the substrate film desirably has transparency as high as possible. Thickness of the substrate film is usually in the  
10 range from 25 to 250  $\mu\text{m}$  or, in most cases, from 50 to 150  $\mu\text{m}$ .

In the preparation of the inventive recording film, the substrate film described above is first provided on one surface with an ink-receptive layer as  
15 the layer (A). It is optional in order to improve adhesion between the substrate surface and the ink-receptive layer that an undercoating layer or a primer layer is formed between the substrate surface and the ink-receptive layer. The undercoating layer  
20 is formed from a resinous material such as saturated polyester resins and urethane resins, of which urethane resins are preferable in respect of good adhesion to the ink-receptive layer thereon. The coating amount of the undercoating layer, when  
25 provided, is in the range from 3 to 15  $\text{g}/\text{m}^2$ .

The ink-receptive layer (A) on the substrate surface or on the undercoating layer mentioned above is formed from a hydrophilic resin composition which comprises: (a) a polyvinyl alcohol resin, (b) a  
30 polyvinyl pyrrolidone resin, (c) an inorganic powder for surface roughening and (d) a crosslinking agent. The polyvinyl alcohol resin has an average degree of polymerization of at least 1000 or, preferably, in the range from 1000 to 3000. When the degree of  
35 polymerization of the polyvinyl alcohol resin is too low, the ink-receptive layer would have low ink absorptivity and decreased water resistance so as

not to exhibit rapid drying of the ink used in ink jet patterning. The polyvinyl alcohol resin can be a completely saponified polyvinyl acetate but is preferably a partial saponification product of a polyvinyl acetate of which the degree of saponification is in the range from 75 to 90%. When the degree of saponification of the polyvinyl alcohol resin is too low, the ink-receptive layer formed by using such a polyvinyl alcohol resin is defective due to a low rate of ink absorption.

The component (b) is a polyvinyl pyrrolidone resin having a molecular weight of at least 40000 or, preferably, in the range from 600000 to 2800000. When the molecular weight of the polyvinyl pyrrolidone resin is too small, the ink-receptive layer is defective due to an unduly large increase in the rate of ink absorption and ink receptivity resulting in retardation of drying of the ink.

The above described polyvinyl alcohol resin as the component (a) and the polyvinyl pyrrolidone resin as the component (b) are contained in the ink-receptive layer in a weight proportion in the range from 9:1 to 4:1 or, preferably, in the range from 7:3 to 5:5. When the amount of the component (a) is too large relative to the component (b), the dryability of the ink in the ink-receptive layer is reduced while, when the amount of the component (a) is too small, the water resistance of the ink-receptive layer is reduced resulting in an appearance of stickiness.

The component (c) in the ink-receptive layer is an inorganic powder for surface roughening which is exemplified by powders of silica, zirconia, clay, kaolin, alumina, titanium dioxide, zeolite, calcium carbonate, barium sulfate, magnesium hydroxide, calcium phosphate and glass. These surface roughening agents can be used either singly or as a combination



of two kinds or more according to need. A preferable surface roughening agent is a combination of a synthetic silica powder and a calcium carbonate powder in a weight ratio from 8:2 to 4:6 or, more preferably, from 7:3 to 5:5 or, still more preferably, in a weight proportion of about 6:4 in respect of good dryability of ink, ink absorptivity, coloration and writing adaptability.

It is preferable to use a surface roughening agent having an average particle diameter in the range from 0.5 to 10  $\mu\text{m}$ . When the particles of the powder are too fine, the surface of the ink-receptive layer sometimes has stickiness so as to cause difficulty in writing with a pen plotter while, when the particles are too coarse, problems are caused in pattern formation with an ink jet means due to a decrease in color reproduction or disorder of the ink jet nozzle resulting in blurring of the imaging line. Assuming that the inorganic surface roughening powders have the same average particle diameter, it is preferable to select one having a larger specific surface area than the others because improvements can be obtained thereby in ink absorptivity and writing adaptability. It is preferable to use a synthetic silica powder having a specific surface area in the range from 500 to 800  $\text{m}^2/\text{g}$  as determined by the simplified BET method and a calcium carbonate powder having a specific surface area in the range from 15000 to 30000  $\text{m}^2/\text{g}$  as determined by the same method. When two kinds or more of surface roughening powders having different specific surface areas are used in combination, it is preferable to combine those having different average particle diameters so that advantages are obtained that the dots formed by an ink jet means may have an approximately circular profile. A preferable example of such a combination is a combination of a synthetic silica powder having an average particle diameter of 2

to 6  $\mu\text{m}$  and a calcium carbonate powder having an average particle diameter of 0.8 to 1.8  $\mu\text{m}$ . In particular, quite satisfactory results can be obtained by the use of a combination of a synthetic silica powder having an average particle diameter of about 6  $\mu\text{m}$  and a calcium carbonate powder having an average particle diameter of about 3.5  $\mu\text{m}$ , a combination of a synthetic silica powder having an average particle diameter of about 3.5  $\mu\text{m}$  and a calcium carbonate powder having an average particle diameter of about 1.4  $\mu\text{m}$  and a combination of two synthetic silica powders having average particle diameters of about 6  $\mu\text{m}$  and about 3.5  $\mu\text{m}$  and a calcium carbonate powder having an average particle diameter of about 1.4  $\mu\text{m}$ .

The amount of the inorganic surface roughening powder as the component (c) in the ink-receptive layer is in the range from 30 to 150 parts by weight or, preferably, from 50 to 120 parts by weight per 100 parts by weight of the total amount of the components (a) and (b). When the amount thereof is too small, fine lines cannot be drawn on the recording layer by a pen plotter with good reproducibility along with a decrease in the water resistance of the recording layer. When the amount thereof is too large, on the other hand, fine lines cannot be drawn by a pen plotter due to blurring of the line or clogging of the pen point and bleeding of ink takes place around the dots formed by an ink jet means so as not to accomplish sharp recording of images.

The crosslinking agent as the component (d) in the ink-receptive layer is preferably a urea resin which is very compatible with the polyvinyl alcohol resin as the component (a) in any appropriate amount so as to give desired water resistance of the layer. The amount of the component (d) is in the range from 5 to 12 parts by weight or, preferably, from 6 to 8

parts by weight per 100 parts by weight of the component (a). When the amount of the component (d) is too small, no full improvement can be obtained in the water resistance and writing adaptability of the recording layer while, when the amount thereof is too large, the ink-receptive layer cannot be imparted with high ink absorptivity.

It is optional that the coating composition for the ink-receptive layer of the inventive recording film contains a catalytic compound in combination with the above described crosslinking agent as the component (d). Suitable catalytic compounds include inorganic ammonium salts such as ammonium chloride, ammonium nitrate and ammonium sulfate. The amount of the catalytic compound, when used, is in the range from 10 to 20% by weight based on the amount of the component (d). When the amount thereof is too small or too large, the writing adaptability and image reproducibility of the inventive recording film cannot be fully improved.

The liquid coating composition for the formation of the ink-receptive layer is prepared by dissolving or dispersing the above described components (a), (b), (c) and (d) in an aqueous medium in appropriate proportions and in such amounts that the solid content of the coating composition is in the range of around 10 to 15% by weight together with various kinds of conventional additives such as surface active agents, lubricants, stabilizers and coloring agents. The thus prepared coating composition is uniformly applied to one surface of a substrate film in a conventional manner followed by drying to form an ink-receptive layer as the layer (A). The ink-receptive layer has a thickness in the range, usually, from 5 to 20  $\mu\text{m}$  or, preferably, from 6 to 15  $\mu\text{m}$ .

The recording film of the present invention is prepared by overcoating the thus obtained

ink-receptive layer on the substrate surface with a dot configuration-controlling layer as the layer (B) to complete the recording layer. The dot configuration-controlling agent contained in the layer (B) is typically exemplified by modified acrylic resins in the form of a quaternary ammonium salt including known copolymers of an alkyl (meth)acrylate and a dialkylaminoalkyl (meth)acrylate converted into a salt. For example, 1:1 by moles copolymers of butyl methacrylate and dimethylaminoethyl methacrylate in the form of a quaternary ammonium salt are available as a commercial product.

The above described dot configuration-controlling agent is dissolved in a lower alcohol or a mixture of a lower alcohol and water to give a coating solution which is uniformly applied onto the ink-receptive layer (A) followed by drying to form a dot configuration-controlling layer (B). It is not always necessary that the layer (B) forms an overcoating layer on the layer (A) to form a layered structure with a definite interface but occurrence of intermixing between the layers (A) and (B) has no particular disadvantage. Accordingly, an alternative way of coating is that the layer (A) is impregnated with a solution of the dot configuration-controlling agent by dipping in the solution followed by drying.

The coating amount of the dot configuration-controlling agent forming the layer (B) is in the range from 3 to 10 g/m<sup>2</sup> in order that the configuration of the recorded dots is nearly a complete circle and bleeding of the ink around the dots is effectively prevented. When the coating amount thereof is too small, sharpness of the recorded images, i.e. pattern resolution, cannot be high enough while, when the amount thereof is too large, a decrease is caused in the ink-absorptivity of the

recording layer and dryability of the ink on the layer.

5 It is essential in the recording film of the invention that the recording film prepared in the above described manner has a surface roughness in the range from 0.8 to 1.5  $\mu\text{m}$  or, preferably, from 1.0 to 1.5  $\mu\text{m}$ . When the surface roughness is too small, a reduction is caused in writing adaptability and, in particular, line density of drawing with a pen plotter 10 along with a reduction in image coloration by an ink jet means. When the surface roughness is too large, on the other hand, problems are caused due to clogging of the pen point with a reduction in writing adaptability and occurrence of a blurred line drawing 15 with a pen plotter and a reduction in image reproducibility by an ink jet means. The above mentioned surface roughness value is a centerline-average height  $R_a$  averaged for measurements repeated 5 times conducted with a 2 cm by 5 cm 20 rectangular test specimen on a three-dimensional surface roughness-form analyzer system (Model Surcom 570A-3DF, manufactured by Tokyo Seimitsu Co.).

The recording layer above described should have a standard rub-off resistance of 150 to 1000 times or, 25 preferably, 170 to 800 times as determined in the manner described below. When the standard rub-off resistance of the recording layer is too low, the pen point of a pen plotter sometimes picks up the coating film by scratching so as to cause clogging of the pen point or a blurred line drawing. A recording layer of 30 which the standard rub-off resistance is too high has poor ink receptivity so that image formation thereon is sometimes incomplete. The standard rub-off resistance here implied is a value obtained by measurement with a peeling/slipping/scratching tester 35 (Model HEIDON 14, manufactured by Heidon Co.) in which the surface of the recording layer is reciprocatingly

rubbed with a fully wet gauze cloth attached to the machine head under a load of 323 g at a velocity of 400 mm/minute to record the number of rubbing times until peeling of the recording layer having an area of at least 1 mm<sup>2</sup> is found on three spots.

It is optional in the recording film of the invention to provide, if necessary, a backing layer as a curl-preventing coating layer onto the reverse surface of the substrate film opposite to the recording layer. The curl-preventing layer is formed from a polymeric resin or a mixture of a polymeric resin and a matte-finish agent in the form of a powder. Suitable polymeric resins include thermoplastic resins, thermosetting resins and photocurable resins such as acrylic resins, urethane resins, polyester resins and polyvinyl chloride resins. Suitable matte-finish agents include inorganic powders such as silica, zirconia, clay, kaolin, alumina, titanium dioxide, zeolite, calcium carbonate, barium sulfate, magnesium hydroxide, calcium phosphate and glass and powders of organic resins such as acrylic resins, urethane resins, polyvinyl chloride resins, benzoguanamine resins and benzoguanamine-melamine-formaldehyde condensation resins. These matte-finish agents should have an average particle diameter in the range from 1 to 20  $\mu\text{m}$  or, preferably, from 2 to 10  $\mu\text{m}$ .

As a variation of the inventive recording film, the substrate film can be provided on both surfaces each with a recording layer. The recording layers on the surfaces can be either of the same type or of different types from one another. For example, only one of the recording layers may be imparted with increased transparency by omitting or decreasing the amount of the matte-finish agent.

The curl-preventing effect by the above mentioned curl-preventing layer can be increased when the

polymeric resin used therein is the same one as used as the components (a) and (b) in the recording layer. The curl-preventing layer has a thickness in the range from 1 to 10  $\mu\text{m}$  or, preferably, from 3 to 7  $\mu\text{m}$ . It is  
5 of course optional that the curl-preventing layer contains various kinds of known additives such as surface active agents, lubricants, stabilizers and coloring agents according to need.

In the following, the method of the invention is  
10 described for information recording using the above described recording film by making reference to the accompanying drawing of which Figure 1 is a block diagram of the instrument system for pattern recording using the inventive recording film and Figures 2 and 3  
15 are each a block diagram for the formation of an image pattern on the recording layer of the inventive recording film.

A base image pattern is first formed in the recording layer by using an ink jet plotter or printer  
20 and then an add-on information pattern is formed thereon using a pen plotter.

Specifically, the first step of the inventive method is formation of a base image pattern in the recording layer by using an ink jet means, which can  
25 be performed by printing an image pattern formed by means of a computer-controlled ink jet plotter or ink jet printer.

Thereafter, an add-on information image is formed using a pen plotter on the base image pattern formed  
30 by an ink jet means. Writing of the add-on information can also be conducted by outputting a computer-formed information image through a computer-controlled pen plotter.

It is of course optional that a single computer  
35 serves to control both the base image formation by an ink jet means and the add-on image formation by a pen

plotter or two separate computers serve to control the respective output instruments.

To describe the inventive method more particularly for the formation of a base image and an  
5 add-on information image, a base image is formed in the recording film by an ink jet means utilizing conventional hardware such as that illustrated in Figure 1 of the accompanying drawing by a block  
10 diagram. In this figure, the "input means" is a device such as a keyboard or mouse for inputting or a scanner which serves to memorize an image pattern prepared separately so as to be available in a computer. The "memory means" in the figure is a  
15 device, such as a hard disk, floppy disk or magneto-optical recording disk, to record information data to be read out when necessary or to record add-on data. The "central processing unit" in the figure serves to conduct data processing for the preparation and modification of the image pattern data,  
20 memorization of the data in the memory device, for the display of the data on a display instrument and outputting of the data. The "display means" serves to exhibit the data and the "output means" includes an ink jet printer and ink jet plotter for printing out  
25 the data prepared or modified in the "central processing unit".

The process for the formation of image patterns on the recording layer of the inventive recording film is illustrated in the block diagrams of Figures 2 and  
30 3 each for a different embodiment of the inventive method. In the block diagram of Figure 2, the first step is an image preparation step in which an image pattern to be formed in the recording layer is provided by using the central processing unit and the  
35 input means and the image pattern data transmitted from the central processing unit is recorded in the memory means. In the image information receiving



step, the image data is received in the output means and the image is modified and worked followed by buildup of the image in the recording layer by an ink jet means using the output means to complete a recording film bearing the desired base image.

In the next step, add-on information data is recorded by a pen plotter on the base image formed by an ink jet means in the recording layer. The hardware used here can be the same as that used in the preceding step with a pen plotter as the output means.

In the block diagram illustrated in Figure 3, a base image prepared in advance and an add-on information image are used and the data thereof is transmitted to the central processing unit through a memory means or input means and the data is worked or modified using the central processing unit and the input means to be completed. Thereafter, the image is formed by an ink jet means in the recording layer through the image output processing step and the image information receiving step to give a recording film bearing the desired base image followed by recording of the add-on information using a pen plotter on the base image formed by an ink jet means.

As is understood from the description given above, the recording film of the invention is advantageous in respect of excellent receptivity and absorption velocity of a water-base ink for the ink jet means and the nearly complete circular form of the dots so as to ensure that a very sharp image is formed on the recording layer. In addition, the recording layer has high water resistance so that the image as formed is free from bleeding of the ink around the dots so as to cause enlargement thereof contributing to the sharpness of the recorded image.

Further, high-density line drawings without blurring can be written by a pen plotter after formation of a base image by an ink jet means without

the patterns due to clogging of the pen point with fragments of the coating layer scratched up thereby. The ink-receptive layer is free from the problems of stickiness due to dissolution by atmospheric moisture or perspiration from hands so as to ensure a high working efficiency.

In the following, the present invention is illustrated in more detail by way of examples, which, however, do not limit the scope of the invention as claimed in any way. In the following examples, in which the term "parts" always refers to "parts by weight", the recording films were evaluated for the following four items (1) to (4) by the respective testing procedures shown.

(1) Dot configuration

Printing was performed using an ink jet plotter (Model Design Jet 750C, manufactured by Hewlett Packard Co.) and the dots were examined by using a stereomicroscope to record the results in three ratings of:

A for a substantially circular form;  
B for a substantially circular form though with some irregularity; and  
C for a form not circular but rather polygonal.

(2) Color reproducibility

(2-1) For an ink jet plotter, printing was performed using the same ink jet plotter as used in (1) above and the reproducibility of each color was visually examined to record the results in three ratings of: A for sharp dots without bleeding of the ink in each color; B for sharp dots but with some bleeding of the ink; and C for blurred dots with heavy bleeding of the ink.

(2-2) For a pen plotter, figure drawing was performed, after printing with an ink jet plotter in the same manner as (2-1) above, on the ink-jet-printed areas using a drafting plotter (Model HP 7595A,

manufactured by Hewlett Packard Co.) with a black ink through a pen point of 0.18 mm diameter and the line drawing was visually examined to record the results in three ratings of:

- 5 A for sharp lines as a whole;  
B for lines somewhat inferior in sharpness; and  
C for unacceptable quality of lines without sharpness.  
(3) Ink dryability

- 10 (3-1) For an ink jet plotter, printed images were formed using the same ink jet plotter as above and the drying behavior of the ink was checked by a finger touch test to record the results in three ratings of:  
A for complete drying within 30 seconds;  
B for complete drying taking 30 to 60 seconds; and  
15 C for complete drying taking more than 60 seconds.

- (3-2) For a pen plotter, figure drawing was performed in the same manner as in (2-2) above and the drying behavior of the ink was checked by a finger touch test to record the results in three ratings of:  
20 A for complete drying within 30 seconds;  
B for complete drying taking 30 to 60 seconds; and  
C for complete drying taking more than 60 seconds.  
(4) Quality of line drawing

- 25 (4-1) For an ink jet plotter, 10 parallel lines each having a line width of 0.176 mm with a space width of 0.220 mm were drawn by using the same ink jet plotter as above with computerization and sharpness of the line drawing and bleeding of the ink around the lines were visually examined to record the results in  
30 three ratings of:  
A for good recognizability of at least 9 lines;  
B for fair recognizability of 7 or 8 lines; and  
C for poor recognizability of only 6 or less lines.

- 35 (4-2) For a pen plotter, 10 lines were drawn with a black ink in the same manner as in (2-2) above and visual inspection was made for the quality of the

imaged lines and interruption of the lines to record the results in three ratings of:

A for a good quality of the line drawing as a whole without bleeding of the ink;

5 B for a fair quality of the line drawing but with some bleeding of the ink; and

C for poor quality of the line drawing or noticeable bleeding of the ink.

Example 1.

10 A liquid coating composition for the ink-receptive layer was prepared by mixing 5 parts of a polyvinyl alcohol resin having an average degree of polymerization of 1700 and a degree of saponification of 88%, 5 parts of a polyvinyl pyrrolidone resin  
15 having an average molecular weight of 630000, 3 parts of a first synthetic silica powder having an average particle diameter of 3.5  $\mu\text{m}$  and a specific surface area of 700  $\text{m}^2/\text{g}$ , 3 parts of a second synthetic silica powder having an average particle diameter of 6.0  $\mu\text{m}$   
20 and a specific surface area of 700  $\text{m}^2/\text{g}$ , 4 parts of a calcium carbonate powder having an average particle diameter of 1.4  $\mu\text{m}$ , 0.3 part of a urea resin, 0.3 part of a 20% by weight aqueous solution of ammonium chloride, 13.5 parts of polypropyleneglycol monomethyl  
25 ether, 20 parts of ethyl alcohol and 80 parts of water.

The above prepared liquid coating composition was applied using a wire-bar coater to one surface of a polyethylene terephthalate film of 100  $\mu\text{m}$  thickness as  
30 a substrate having a 1.0  $\mu\text{m}$  thick undercoating layer of a urethane resin followed by drying at 130 °C for 5 minutes to form an ink-receptive layer having a thickness of 10  $\mu\text{m}$ .

35 Separately, a liquid coating composition for a dot configuration-controlling layer was prepared by dispersing 1.0 part of a modified acrylic resin in the form of a quaternary ammonium salt (Surftoma CP-2000,

a product of Mitsubishi Petrochemical Co.) in a mixture of 10.0 parts of ethyl alcohol and 89.0 parts of water and this coating solution was applied to the surface of the ink-receptive layer followed by drying to form a dot configurationcontrolling layer, of which the coating amount with the modified acrylic resin was 4 g/m<sup>2</sup>.

Further, the reverse surface of the substrate film opposite to the ink-receptive layer was coated with a matte-finish coating liquid prepared from 20 parts of a copolymeric acrylic resin as a binder, 10 parts of a synthetic silica powder having an average particle diameter of 3.5  $\mu$ m as a matte-finish agent and 70 parts of water followed by heating at 30 °C for 2 minutes to form a matte-finish layer having a thickness of 5  $\mu$ m.

Table 1 below shows the results of the evaluation tests undertaken for the thus prepared recording film as well as the surface roughness of the recording layer in  $\mu$ m and the standard rub-off resistance in times of rubbing together with the results of testing for other Examples and Comparative Examples.

Example 2.

The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared from: 6 parts of the polyvinyl alcohol resin; 4 parts of the polyvinyl pyrrolidone resin; 3 parts each of the first and second synthetic silica powders; 4 parts of the calcium carbonate powder; 0.36 part of the urea resin; 0.36 part of the ammonium chloride solution; 20 parts of ethyl alcohol; 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

Example 3.

The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared from:

- 5 7 parts of the polyvinyl alcohol resin;
- 3 parts of the polyvinyl pyrrolidone resin;
- 3 parts each of the first and second synthetic silica powders;
- 4 parts of the calcium carbonate powder;
- 10 0.42 part of the urea resin;
- 0.42 part of the ammonium chloride solution;
- 20 parts of ethyl alcohol;
- 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

15 Example 4.

The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared from:

- 20 6 parts of the polyvinyl alcohol resin;
- 4 parts of the polyvinyl pyrrolidone resin;
- 6 parts of the first synthetic silica powder;
- 4 parts of the calcium carbonate powder;
- 0.36 part of the urea resin;
- 25 0.36 part of the ammonium chloride solution;
- 20 parts of ethyl alcohol;
- 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

Example 5.

- 30 The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared from:

- 5.4 parts of the polyvinyl alcohol resin;
- 35 3.6 parts of the polyvinyl pyrrolidone resin;
- 3.6 parts each of the first and second synthetic silica powders;

- 4.4 parts of the calcium carbonate powder;
- 0.32 part of the urea resin;
- 0.32 part of the ammonium chloride solution;
- 20 parts of ethyl alcohol;
- 5 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

Example 6.

The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared from:

- 6.6 parts of the polyvinyl alcohol resin;
- 4.4 parts of the polyvinyl pyrrolidone resin;
- 2.7 parts each of the first and second synthetic
- 15 silica powders;
- 3.6 parts of the calcium carbonate powder;
- 0.4 part of the urea resin;
- 0.4 part of the ammonium chloride solution;
- 20 parts of ethyl alcohol;
- 20 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

Comparative Example 1.

The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared, by omitting the polyvinyl alcohol resin, from:

- 10 parts of the polyvinyl pyrrolidone resin;
- 6 parts of the first synthetic silica powder;
- 4 parts of the calcium carbonate powder;
- 30 0.24 part of the urea resin;
- 0.24 part of the ammonium chloride solution;
- 20 parts of ethyl alcohol;
- 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

35 Comparative Example 2.

The experimental procedure was substantially the same as in Example 1 except that the liquid coating

composition for the ink-receptive layer was prepared, by omitting the polyvinyl pyrrolidone resin, from:

10 parts of the polyvinyl alcohol resin;

6 parts of the first synthetic silica powder;

5 4 parts of the calcium carbonate powder;

0.6 part of the urea resin;

0.6 part of the ammonium chloride solution;

20 parts of ethyl alcohol;

10 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

Comparative Example 3.

The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared, by omitting the synthetic silica powders and calcium carbonate powder, from:

6 parts of the polyvinyl alcohol resin;

4 parts of the polyvinyl pyrrolidone resin;

1 part of the urea resin;

20 0.36 part of the ammonium chloride solution;

20 parts of ethyl alcohol;

13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.

Comparative Example 4.

25 The experimental procedure was substantially the same as in Example 1 except that the liquid coating composition for the ink-receptive layer was prepared, by omitting the urea resin and ammonium chloride solution, from:

30 6 parts of the polyvinyl alcohol resin;

4 parts of the polyvinyl pyrrolidone resin;

6 part of the first synthetic silica powder;

20 parts of ethyl alcohol;

35 13.5 parts of the polypropyleneglycol monomethyl ether; and 80 parts of water.



T a b l e 1

	Sur- face rough- ness, $\mu\text{m}$	Stan- dard rub-off resist- ance, times	Dot con- fig- ura- tion	Color repro- ducibility		Ink dry- ability		Quality of line drawing	
				ink jet plot- ter	pen plot- ter	ink jet plot- ter	pen plot- ter	ink jet plot- ter	pen plot- ter
Exam- ple	1 1.3	200	A	A	A	A	A	A	A
	2 1.3	200	A	A	A	A	A	A	A
	3 1.3	200	A	A	A	A	A	A	A
	4 1.3	200	A	A	A	A	A	A	A
	5 1.3	200	A	A	A	A	A	A	A
	6 1.3	200	A	A	A	A	A	A	A
Com- para- tive Exam- ple	1 1.2	20	B	B	C	B	-	B	C
	2 1.2	200	A	B	C	C	B	B	B
	3 0.3	30	A	A	C	B	-	A	C
	4 1.2	2	A	A	C	A	-	A	C

## CLAIMS:

1. A recording film which comprises, as an integral  
5 layered film: (1) a substrate film; and (2) a  
composite recording layer consisting of  
(A) an ink-receptive layer formed on one surface  
of the substrate film, the layer consisting of (a) a  
polyvinyl alcohol resin, (b) a polyvinyl pyrrolidone  
10 resin, (c) an inorganic powder for surface roughening  
and (d) a crosslinking agent, and  
(B) an overcoating layer containing a dot  
configuration-controlling agent formed on the  
ink-receptive layer, the surface of the recording  
15 layer having a surface roughness in the range from 0.8  
to 1.5  $\mu\text{m}$ .
2. The recording film according to claim 1 in which  
the weight proportion of the component (a) and  
20 component (b) in the ink-receptive layer is in the  
range from 9:1 to 4:6.
3. The recording film according to claim 1 in which  
the amount of the component (c) in the ink-receptive  
25 layer is in the range from 30 to 150 parts by weight  
per 100 parts by weight of the total amount of the  
components (a) and (b).
4. The recording film according to claim 1 in which  
30 the component (c) in the ink-receptive layer is a  
combination of a synthetic silica powder and a calcium  
carbonate powder in a weight proportion in the range  
from 8:2 to 4:6.
5. The recording film according to claim 1 in which  
35 the component (d) in the ink-receptive layer is a urea  
resin.

6. The recording film according to claim 1 in which the dot configuration-controlling agent in the layer (B) is an acrylic resin in the form of a quaternary ammonium salt.
7. The recording film according to claim 1 in which the amount of the component (d) in the ink-receptive layer is in the range from 5 to 12 parts by weight per 100 parts by weight of the component (a).
8. The recording film according to claim 1 in which the thickness of the ink-receptive layer is in the range from 5 to 20  $\mu\text{m}$ .
9. The recording film according to claim 1 in which the coating amount of the layer (B) is such that the layer contains from 3 to 10  $\text{g/m}^2$  of the dot configuration-controlling agent.
10. A method for dual recording of image patterns in a recording film comprising, as an integral layered film: (1) a substrate film; and (2) a composite recording layer consisting of
- (A) an ink-receptive layer formed on one surface of the substrate film, the layer consisting of (a) a polyvinyl alcohol resin, (b) a polyvinyl pyrrolidone resin, (c) an inorganic powder for surface roughening and (d) a crosslinking agent, and
- (B) an overcoating layer containing a dot configuration-controlling agent formed on the ink-receptive layer, the surface of the recording layer having a surface roughness in the range from 0.8 to 1.5  $\mu\text{m}$ , which comprises the steps of: i) forming a base image pattern in the recording layer of the recording film by an ink jet patterning means; and ii)

forming an add-on image pattern on the surface of the recording layer by writing with a pen plotter.

11. A recording film as claimed in claim 1  
5 substantially as hereinbefore described in any one of the Examples.



Application No: GB 9718613.4  
Claims searched: 1-11

Examiner: Richard Kennell  
Date of search: 19 November 1997

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK Cl (Ed.O): B2E (EKB, EM, EN, EQ)  
Int Cl (Ed.6): B41M 1/30 1/36  
Other: Online: WPI, JAPIO, CLAIMS

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 2129333 A (CANON K.K.), see page 3 lines 40-46, and use of filler for surface roughness	1,10 at least
Y	EP 0198636 A (I.C.I.), see page 4 lines 7-16, page 5 line 2 - page 6 line 30 and Examples 2 - 4	1,10 at least
Y	EP 0125113 A (TEKTRONIX INC.), whole document	1,10 at least
Y	US 4592951 A (VIOLA), whole document	1,10 at least
Y	WPI Abstract Accession No 96-338194/34 & JP 080156396 A (SOMAR CORP.), see abstract	1,10 at least
Y	WPI Abstract Accession No 95-299054/39 & JP 070195894 A (SOMAR CORP.), see abstract	1,10 at least
Y	WPI Abstract Accession No 90-078637/11 & JP 020030582 A (SOMAR CORP.)	1,10 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.